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The effect of $SrSO_4$ and $BaSO_4$ on the corrosion and wetting by molten aluminum alloys of mullite ceramics

M.N. Ibarra Castro *, J.M. Almanza Robles, D.A. Cortés Hernandez,
J.C. Escobedo Bocardo, J. Torres Torres

CINVESTAV – Unidad Saltillo, Carretera Saltillo-Monterrey Km. 13.5 Ado, Postal 663, Saltillo, Coahuila 25000, Mexico

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Abstract

In order to improve the corrosion resistance of aluminosilicate refractories by molten aluminum, $SrSO_4$ and $BaSO_4$ powders were used. Mullite substrates with and without addition of 20 wt.% $SrSO_4$ or $BaSO_4$ were sintered at 1400 °C for 6 h. Corrosion and wetting experiments with molten pure Al and Al–7.5Si were carried out at 900 °C for 24 h and 900 °C for 2 h, respectively. The corrosion layer was thicker in the mullite sample ($\geq$2 mm) than that of the $SrSO_4$- or $BaSO_4$-containing mullite samples ($<$50 μm). The contact angles for mullite samples containing $SrSO_4$ or $BaSO_4$ were higher ($\approx$118° and 149°) than those of the mullite sample ($\approx$109° and 127°), with both pure aluminum and Al–7Si alloy. This increase in the contact angle improves the corrosion resistance in mullite samples by means of non-wetting effect.

Keywords: C. Corrosion; D. Mullite; Celsian; Aluminum wetting

1. Introduction

The primary requirement of a refractory in contact with molten aluminum is to maximize the furnace operating life. In addition, the refractory must contain the molten metal and maintain the metal quality [1]. Alumina and spinel [2] have shown high chemical stability with molten aluminum. At the same time, SiC has been tested as an additive in the refractory concrete composition [2]. The use of SiC in the concrete composition optimizes the resistance to alkalis and contributes to prevent aluminum wetting on the surface of the refractories. However, these materials are usually expensive.

The aluminosilicate refractories have been widely employed in the aluminum industry due to their good mechanical properties at the service temperature and good thermal resistance; they are also inexpensive and widely available. Such refractories, however, degrade via reaction with molten aluminum alloys due to the strong reducing effect of aluminum [3]. In general, the area affected by molten aluminum in a refractory material is visible by black appearance. Sometimes, the corroded area appears as a composite material, composed mainly of small grains of corundum surrounded by an interconnected metallic network [4]. The alumina layer formed and the original refractory have different thermal expansion coefficients thus, due to thermal fluctuations this alumina layer separates from the refractory, leading to an increase in the corrosion rate [2].

One condition for the reaction to begin is that the refractory has to be wet by the molten metal [5]. Wetting is defined as the ability of a liquid to totally cover a solid substrate, and it is expressed by the contact angle between the liquid droplet and the substrate [6] and it is categorized as reactive and non-reactive wetting [7]. In a non-reactive system wetting occurs rapidly (10^{-4} to 0.1 s), while in reactive systems, the equilibrium wetting could occur over a long time interval, often hours. In reactive systems, wetting is interactively coupled with the reaction kinetics of the solid refractory and the molten metal; consequently the spreading behavior of metal droplet becomes complex and less clear. The wetting would be also influenced by the presence of the alloying elements and the other constituents of the refractory [7].

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* Corresponding author. Tel.: +52 844 4389600; fax: +52 844 4389610.
E-mail addresses: mnic79@hotmail.com (M.N. Ibarra Castro),
manuel.almanza@cinvestav.edu.mx (J.M. Almanza Robles),
dora.cortes@cinvestav.edu.mx (D.A. Cortés Hernandez),
jose.escobedo@cinvestav.edu.mx (J.C. Escobedo Bocardo),
jesus.torres@cinvestav.edu.mx (J. Torres Torres).

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In order to enhance the corrosion resistance and reduce wetting of aluminosilicate refractory materials by molten aluminum, several additives have been used as non-wetting agents, such as fluorite (CaF_2) [1–3,8,9], aluminum fluoride (AlF_3) [8,9], ceria (Ce_2O_3) [10] and barite ($BaSO_4$) [1–3,8,9]. The fluoride additives (AlF_3 and CaF_2) act as mineralizers, favoring the mullite formation during high-temperature firing of aluminosilicate materials [8]. The ceria (Ce_2O_3) acts as catalyzer or mineralizer that alters the refractory microstructure and may assist in devitrification of the matrix to produce a more resistant crystalline material [10].

Recently, there is a particular interest in studying the role of barium sulfate ($BaSO_4$) addition on the corrosion resistance increase of refractories. Barite, by reacting with alumina and silica fine particles of the refractories, forms hexa-celsian and/or celsian ($BaSi_2Al_2O_8$) at the firing temperature ranging between 900 and 1200 °C. The formation of $BaSi_2Al_2O_8$ may explain the improved corrosion resistance [8].

The influence of MgO, CaO and BaO additions on Al_2O_3–SiO_2 ceramics has been also investigated [11]. The results suggested that the addition of these oxides defines the microstructure of sintered ceramics, moreover, the reaction of Al_2O_3–SiO_2 ceramics with MgO, CaO and BaO additives forms $Mg_2Al_4Si_5O_{18}$, $CaSi_2Al_2O_8$ and $BaSi_2Al_2O_8$ and such phases show a low reactivity with molten aluminum.

On the other hand, it has been reported [7] that wetting of ceramics materials with molten aluminum decreases by addition of non-wetting agents. Introducing these agents, higher contact angles could be obtained. However, the nature of the non-wetting agents used in that study was not specified.

So far, the corrosion mechanisms of aluminosilicate refractories and the effect of non-wetting agents with aluminum alloys are not deeply known. Addition, $SrSO_4$ has not been employed as non-wetting agent in refractory materials. This work aims to determine the influence of alkaline-earth sulfates $SrSO_4$ and $BaSO_4$ added to mullite ceramics on the reaction with aluminum alloys.

2. Experimental

Pure aluminum (99.74% purity) and a commercial aluminum alloy containing about 7.5 wt.%. Si as the major alloying element were used in this study. According to the chemical analysis, the aluminum alloy is composed (wt.%) of 7.58Si, 3.23Cu, 1.85Zn, 0.952Fe, 0.28Mn, 0.0403Mg, 0.0403Pb, and the remainder Al.

Mullite powder (Virginia K, mesh # 325) and alkaline-earth sulfates (Grade 99+% Aldrich) were employed to prepare mullite–20 wt.% $SrSO_4$ and mullite–20 wt.% $BaSO_4$ mixtures. Powder mixtures were homogenized in a ball mill in acetone for 4 h. The mixtures were dried at 60 °C for 24 h and ground in a mortar to eliminate agglomerates. Pellets of mullite powders with and without sulfates addition of 2 and 4 cm in diameter were prepared by uniaxial pressing at 100 and 78 MPa, respectively. The pellets were sintered at 1400 °C for 6 h. Sintered samples were analyzed by XRD.

For corrosion experiments, mullite samples and 500 g of aluminum were placed inside a high alumina crucible at room temperature and heated at 900 °C for 24 h. The substrates, before and after corrosion experiments, were cross-sectioned and ground using SiC papers of 320, 500, 800, 1200 and 2400 grit. The final polishing was done using a 3 μm diamond paste. Samples were carbon-coated and analyzed by SEM.

Wetting experiments were carried out in a tight closed tubular furnace using the sessile drop test. Cubes (L = 1 cm) of the aluminum alloys samples were cut, grounded using SiC grind papers # 80 and 800 and cleaned with acetone. Aluminum cubes and Zr sponge were placed inside the furnace tube, which was equipped with a transparent window at one end. All wetting experiments were conducted under ultra-high purity argon (99.999%) atmosphere, with a continuous flow rate (5 L/min). The furnace temperature was programmed to increase at 20 °C/min reaching 900 °C in 2 h. A digital video camera was used to record the shape of the drop at regular intervals (every 5 min). Images for angle contact estimations were captured from the video taken at the hold temperature for 2 h. Contact angles were determined drawing up tangent lines in the contact zone between the liquid drop and the ceramic substrate.

Additionally, roughness of the substrates surface before wetting experiments was measured using a rugosimeter Mitutoyo model Suit Test-211.

3. Results and discussion

Fig. 1 shows the XRD patterns of mixtures of mullite–20 wt.% $SrSO_4$ and mullite–20 wt.% $BaSO_4$ sintered at 1400 °C for 6 h. The mullite–20 wt.% $SrSO_4$ sample showed the presence of mullite and monoclinic $SrSi_2Al_2O_8$. For mullite–20 wt.% $BaSO_4$ sample, mullite and hexagonal $BaSi_2Al_2O_8$ were detected. It has been reported that [8] the $BaSi_2Al_2O_8$ formation, by $BaSO_4$ addition, reduces the amount of free silica in the matrix and should, consequently, improve

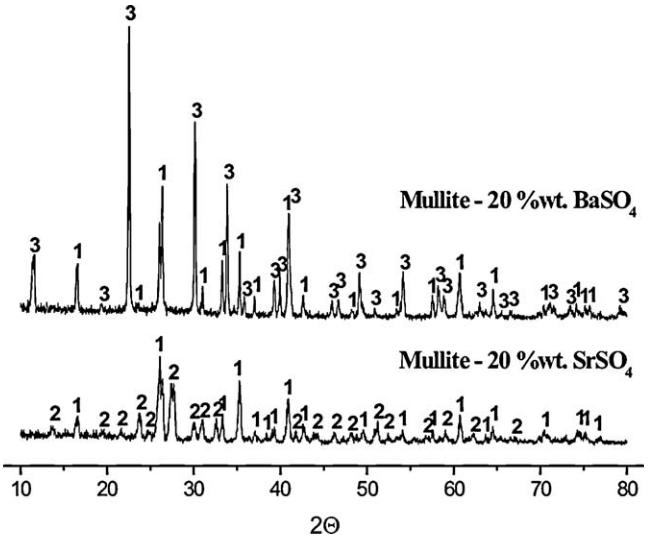

Fig. 1. XRD patterns of mullite–20 wt.% $SrSO_4$ and mullite–20 wt.% $BaSO_4$ samples sintered at 1400 °C for 6 h. (1) Mullite, (2) $SrSi_2Al_2O_8$ and (3) $BaSi_2Al_2O_8$.

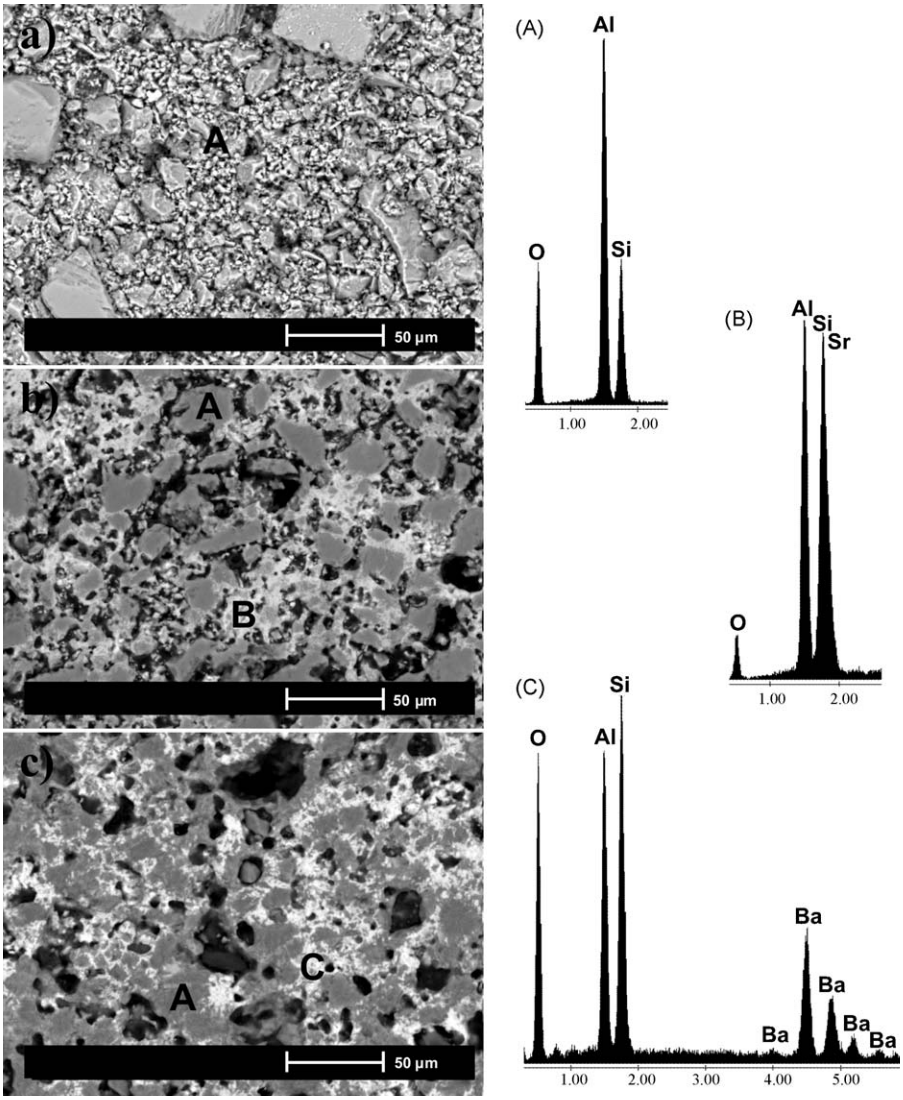

Fig. 2. SEM micrographs and EDS analysis of samples sintered at 1400 °C for 6 h. (a) Mullite, (b) mullite–20 wt.% $SrSO_4$ and (c) mullite–20 wt.% $BaSO_4$.

the corrosion resistance of the refractory. On the other hand, monoclinic $SrSi_2Al_2O_8$ could be an excellent candidate for refractory applications due to its low thermal expansion and high melting temperature [12].

Fig. 2 presents SEM micrographs and EDS analysis of mullite samples with and without addition of $SrSO_4$ or $BaSO_4$ (20 wt.%) sintered at 1400 °C for 6 h. The matrix phase observed in Fig. 2a–c corresponds to mullite, and white phases observed in Fig. 2b and c correspond to the Sr and Ba silicoaluminates detected by XRD (Fig. 1).

Fig. 2 shows also that $SrSO_4$- or $BaSO_4$-containing mullite samples present more porosity than mullite sample. It has been reported [13] that the presence of a glassy phase composed mainly of BaO and SiO_2 formed by addition of 9 wt.% of BaO to aluminosilicate materials, leads to a dense microstructure. In general, the addition of 9 wt.% BaO to aluminosilicate refractories drastically decreases the coarse porosity and seemingly closes the fine pores. Further additions of BaO gradually reduce the glassy phase and celsian, $BaSi_2Al_2O_8$, becomes the main crystalline phase, while alumina appears as a secondary phase. The coarse porosity is generally diminished but the formation of celsian creates tiny pores and lowers the shrinkage [13].

Fig. 3 shows SEM micrographs for mullite samples with and without addition of $SrSO_4$ or $BaSO_4$ (20 wt.%) after corrosion experiments with pure aluminum and Al–7.5 wt.% Si at 900 °C for 24 h. A continuous alumina layer (thickness $\approx$ 2 mm) can be observed for mullite sample after corrosion experiment with pure aluminum (Fig. 3a). The mullite sample was completely corroded after being in contact with Al–7.5Si (Fig. 3b). The change in morphology of the sample due to corrosion effect is evident.

Continuous alumina layers ($\approx$20 µm) were detected in the interface between aluminum alloy and ceramic substrate for the $SrSO_4$-containing mullite samples (Fig. 3c and d) after corrosion experiments with pure Al and Al–7.5Si. On the other hand, no corrosion was observed for $BaSO_4$-containing mullite sample after corrosion experiment with pure Al (Fig. 3e); however, several localized reaction-zones ($\approx$50 µm) were found for the $BaSO_4$-containing mullite

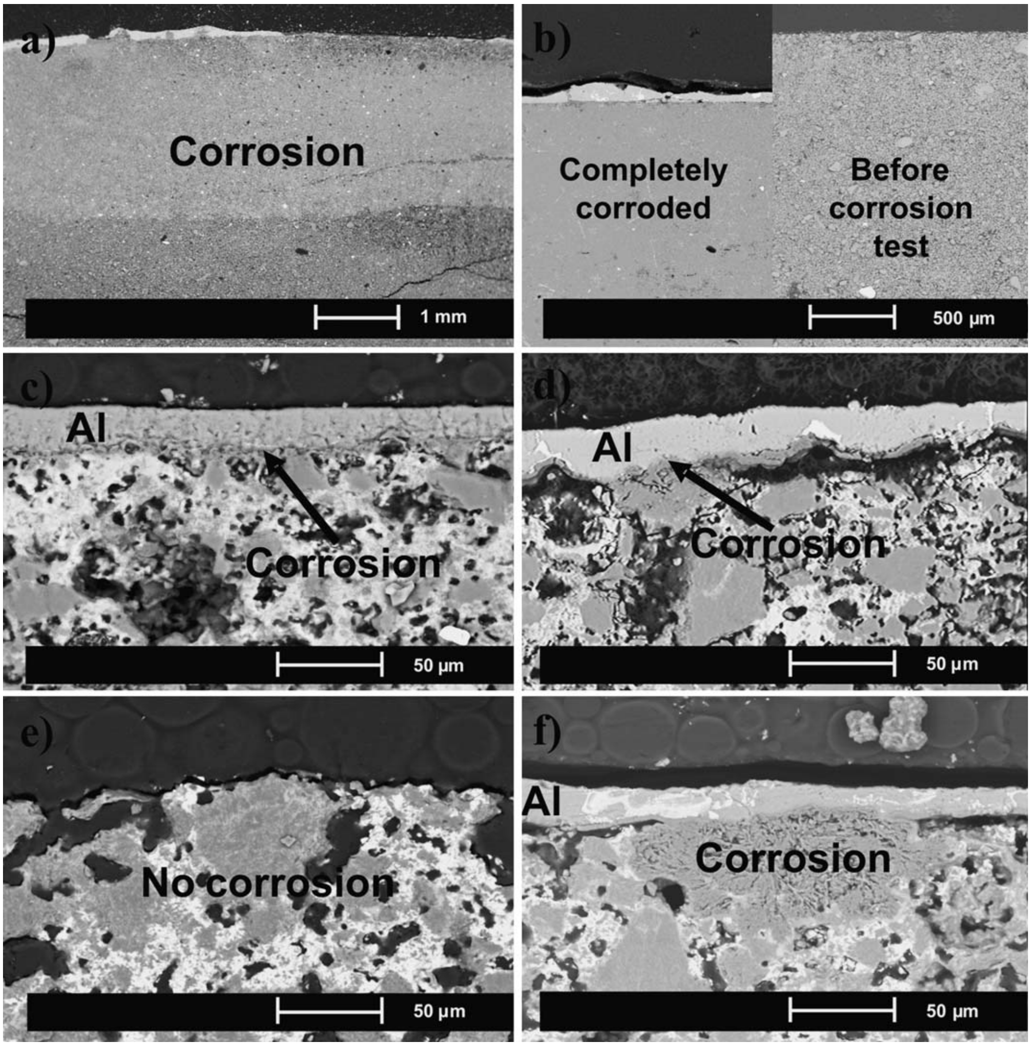

Fig. 3. SEM micrographs of ceramic substrates after corrosion experiment at 900 °C for 24 h. (a) Mullite/pure Al, (b) mullite/Al–7.5Si (before and after corrosion test), (c) mullite–20 wt.% $SrSO_4$/pure Al, (d) mullite–20 wt.% $SrSO_4$/Al–7.5Si, (e) mullite–20 wt.% $BaSO_4$/pure Al and (f) mullite–20 wt.% $BaSO_4$/Al–7.5Si.

sample after being in contact with Al–7.5Si (Fig. 3f). No reaction was observed between high alumina crucible and aluminum alloy.

The microstructure analysis at higher magnifications for $SrSO_4$- or $BaSO_4$-containing mullite samples (Fig. 4) that corresponds to Fig. 3c, d and f showed the presence of alumina in the reaction-zone. The EDS spectra correspond to Fig. 4a; however, all samples presented similar EDS results. There was not evidence that aluminum reacted with Sr and Ba Celsian since there was not Sr and Ba detected in the aluminum layer. This indicates that aluminum reduced only the mullite phase forming alumina as a reaction product.

In general, an increase in corrosion resistance with aluminum alloys was observed for $SrSO_4$- or $BaSO_4$-containing mullite samples. Mullite samples containing $SrSO_4$ or $BaSO_4$ presented alumina layers smaller than those on mullite samples.

Fig. 5 shows a comparison of contact angles between mullite samples with and without addition of $SrSO_4$ or $BaSO_4$ (20 wt.%) obtained from wetting experiments at 900 °C for 2 h. with pure Al and Al–7.5Si. Mullite samples without $SrSO_4$ or $BaSO_4$ additions, in contact with pure Al and Al–7.5Si, showed contact angles of $109^\circ \pm 3.1$ and $126^\circ \pm 3.2$, respectively. Contact angles for $SrSO_4$-containing mullite samples in contact with pure Al and Al–7.5Si were $118^\circ \pm 2.0$ and $149^\circ \pm 2.0$, respectively. Contact angles for $BaSO_4$-containing mullite samples in contact with pure Al and Al–7.5Si were $118^\circ \pm 2.4$ and $148^\circ \pm 2.7$, respectively. On the other hand, roughness values ($R_{(a)}\mu_{in}$) for mullite, mullite–$SrSO_4$ and mullite–$BaSO_4$ samples were 52.6, 80.2 and 107.6, respectively. In general, the surface with higher roughness values showed higher wetting angles, due to that the surface imperfections avoid the spreading of the liquid [14]. In general, the addition of $SrSO_4$ or $BaSO_4$ and high roughness decreased the wetting as indicated by higher contact angles.

One major problem concerning the measurement of the wetting angle of aluminum and its alloys is that these metals have high affinity towards oxygen. It is hence difficult to obtain an oxide-free surface in aluminum, and the presence of this oxide film will strongly influence the measurement [5].

Fig. 5 also shows that the angles of contact obtained in the wetting experiments carried out with Al–7.5Si are higher than contact angles obtained in the wetting experiments carried out

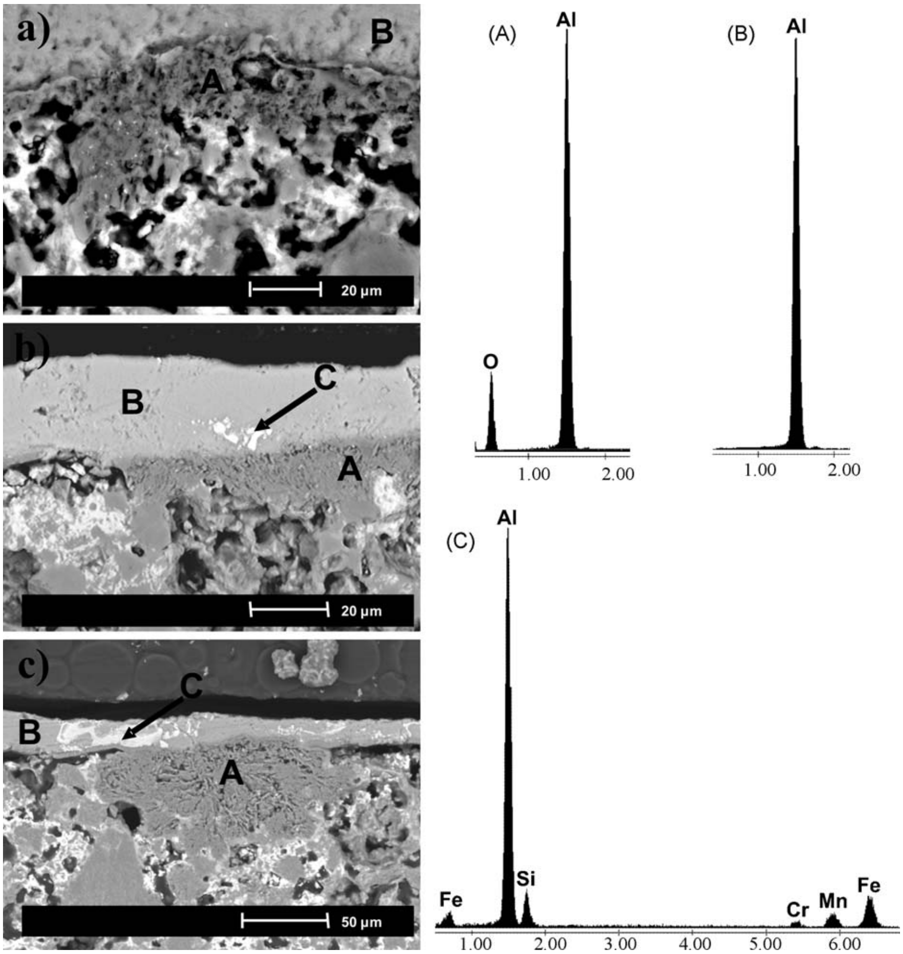

Fig. 4. SEM micrographs and EDS analysis of ceramic substrates after corrosion experiment at 900 °C for 24 h. (a) Mullite–20 wt.% $SrSO_4$/pure Al, (b) mullite–20 wt.% $SrSO_4$/Al–7.5Si and (c) mullita–20 wt.% $BaSO_4$/Al–7.5Si.

with pure aluminum. In general, molten metals in contact with ceramics are ''non-equilibrium'' systems where a reaction and mass transference through the interface occurs [15], this aspect has a strong influence on wetting. The wetting in the Al–SiO_2 system [16] cannot be truly reflected by the contact angles alone; besides physical aspects, the reaction between molten aluminum and the ceramic substrate and molten aluminum penetration is also significant. In general angles of contact obtained in the wetting experiments in this work, carried out with pure aluminum and Al–7.5Si are in the range of the results reported in the literature for experiments realized under similar conditions [7,16,17]. Due to that contact angle in influence by several factors such as, rugosity, chemical reaction, bonding structure, crystallographic orientation, adsorcion, etc. [18], in this work the change in contact angles only can be analyzed in a general way. Samples containing $BaSO_4$ and $SrSO_4$ showed higher contact angles than those for mullite indicating a non-wetting effect by this addition.

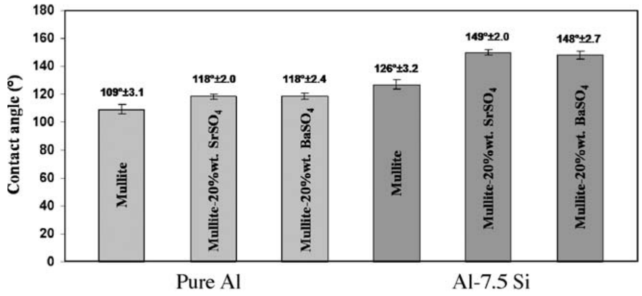

Fig. 5. Comparison of contact angles between mullite samples with and without addition of $SrSO_4$ or $BaSO_4$ (20 wt.%) in contact with pure Al or Al–7.5Si.

Equilibrium thermodynamic calculations were performed using the FACTSage program for the systems Al–$Al_6Si_2O_{13}$, Al–$SrAl_2Si_2O_8$ and Al–$BaAl_2Si_2O_8$ at 900 °C. The results showed that mullite and strontium celsian were not stable in contact with aluminum. Mullite reacted to form alumina and Si while $SrAl_2Si_2O_8$ reacted with aluminum to form Al_2O_3, Si and $SrSiO_3$. EDS analysis (Fig. 4) showed the formation of alumina as thermodynamic calculations predicted, however no evidence of the formation of $SrSiO_3$ was found. It was expected that $SrAl_2Si_2O_8$ showed no chemical stability in contact with liquid aluminum; however as contact angles showed the wettability played also a role in order to improve corrosion resistance. As thermodynamic calculations and wettability experiments indicated, the composite mullite–$BaAl_2Si_2O_8$, showed the best corrosion resistance for liquid aluminum.

4. Conclusions

In summary, it can be deduced that the addition of $SrSO_4$ or $BaSO_4$ are affective for increasing the corrosion resistance and decreasing the wettability by aluminum alloys (which becomes evident in Figs. 3 and 5). XRD analysis showed the presence of $SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$ in mullita samples containing $SrSO_4$ and $BaSO_4$ (20 wt.%), respectively. Addition of $SrSO_4$ or $BaSO_4$ improved corrosion resistance on mullite ceramics with molten aluminum alloys and showed higher contact angles than those of the mullite samples. Ceramic substrates with higher roughness values showed higher wetting angles. Thermodynamic calculations and wettability experiments indicated that the composite mullite–$BaAl_2Si_2O_8$, showed the best corrosion resistance for liquid aluminum.

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